WO 2005/078044 PCT/IB2005/000061

#### **COATED ABRASIVES**

## **BACKGROUND OF THE INVENTION**

This invention relates to coated abrasives, a process for their production, and to coated abrasives for use in abrasive-containing tools.

Abrasive particles such as diamond and cubic boron nitride are commonly used in cutting, grinding, drilling, sawing and polishing applications. In such applications, abrasive particles are mixed with metal powder mixes, then sintered at high temperatures to form bonded cutting elements. Typical bond matrices contain iron, cobalt, copper, nickel and/or alloys thereof.

Common problems in applications are retention of particles in the bond matrix, and resistance against oxidative attack during the sintering process and the subsequent application.

These problems are commonly addressed by coating the abrasive particles with metals or alloys which bond chemically to the particle, and alloy to the bond matrix. Typically, chemical vapour deposition (CVD) or physical vapour deposition (PVD sputter coating) techniques are used. Titanium carbide is an example of a material that has been proposed as a coating for abrasive particles, because of its good adhesion to diamond. Chromium carbide is a similar coating material that can be used.

- 2-

A problem with the use of titanium carbide coatings is that in order for the coating to protect the diamond particles, it has to form a barrier between the bond matrix and the particles. In other words, it should be impermeable and dense, so that components of the bond matrix are unable to pass through and make contact with the particle surface. One way the components could pass through the coating is by solid-state diffusion through the coating. Alternatively, if the coating is incomplete, cracked or porous, components may pass through the coating to reach the particle surface. A coating may initially be dense and impermeable, but during the sintering process, a phase change may occur due to alloying with the bond matrix, for example, which results in the formation of a less dense alloy, or perhaps a porous coating, which allows passage of the bond matrix components through the coating to the particle surface. Titanium carbide coatings often do not form good barriers, particularly in aggressive sintering conditions.

## **SUMMARY OF THE INVENTION**

A coated super-hard abrasive comprising a core of super-hard abrasive material, an inner layer of a metal carbide, nitride, boride, carbonitride or boronitride chemically bonded to an outer surface of the super-hard abrasive material and an outer layer of a metal, metal alloy or a combination of metals or metal alloys deposited on the inner layer.

Examples of metals or metal alloys that can be applied as an outer layer include metals from group IVa, Va or VIa transition metals, including tungsten, titanium, chromium, molybdenum, and zirconium, and metals from the first row transition metals (Ti to Cu), particularly the non magnetic metals or alloys of these that are amenable to magnetron sputtering, and elements from groups IIIb and IVb of the periodic table, such as B, AI, Si. Alloys might include the metals mentioned above with metals selected from the platinum group metals and metals from group Ib. Examples are

aluminium-, copper- or nickel- titanium. An example of a non magnetic alloy from the first row transition metals is nickel – 20 weight % chromium.

The outer layer is preferably applied by physical vapour deposition, in particular by PVD sputter coating.

The super-hard abrasive material may be diamond or cBN based, and may include diamond or cBN grit, PCD substrates, PcBN substrates, thermally stable PCD (TSPCD) substrates, CVD diamond film, single crystal diamond substrates.

The inner layer is formed from an element capable of forming (singly or in combination) carbides, nitrides or borides to the surface(s) of the abrasive material when applied as an inner layer using a hot coating process. Typically these elements come from groups IVa, Va, Vla, IIIb and IVb of the periodic table and include examples such as Ti, Cr, Zr, Mo, Ta, W, Al, B and Si. The inner layer is preferably a titanium or chromium carbide coating in the case of a diamond abrasive core, or a titanium or chromium nitride, boride or boronitride coating in the case of a cBN abrasive core.

The properties of the metal layer may be tailored for better compatibility with the inner layer or for better bonding with metal bond matrices.

### **DESCRIPTION OF PREFERRED EMBODIMENTS**

Whilst the invention extends to various forms of coated abrasive material, it will in the most part be described with reference to the coating of diamond grit for convenience.

Ti in the form of titanium carbide or titanium nitrides, borides and boronitrides have been shown to be useful coating materials for diamond and cBN substrates, respectively. They are particularly useful because of their ability to bind chemically to the substrate and to protect the substrate.

However, as has been mentioned previously, they are not suitable in some applications, particularly where they are sintered in aggressive sintering conditions. They are also prone to problems with bonding properly with the bond matrix.

It has been found that the advantages of titanium coatings can be extended to other applications where an outer metal coating is applied over the titanium coating layer. This is particularly the case where the titanium coating is prone to deterioration and where there is poor bonding with the metal matrix.

It is especially useful in the making of diamond impregnated tools such as segments for saw blades, drills, beads for diamond wires especially where high amounts of bronze or copper limit the usefulness of titanium carbide coatings, the making of brazed diamond layer tools such as brazed diamond wire beads, the making of diamond containing metal matrix composites, brazing of diamond materials such as affixing TSPCD, PCD and diamond drillstones to a drill body, affixing CVD, monocrystal, TSPCD and PCD to a saw blade, tool post, drill body and the like.

Additionally, the coated diamond impregnated tools yield improved performance, such as longer tool life and higher productivity. Coated diamond particles or substrates of the invention for brazing applications allow the use of simple brazes that work in air as opposed to active brazes containing Ti which require the exclusion of oxygen.

The coated abrasive particles are preferably formed using a hot coating process for applying the inner layer and a low temperature CVD or PVD process for applying the outer layer.

The diamond grit particles are those used conventionally in the manufacturing of metal bonded tools. They are generally uniformly sized, typically 0.1 to 10 mm. Examples of such diamond grit particles include: Micron grit 0.1 to 60 micron, wheel grit 40 micron to 200 micron, saw grit

180 micron to 2 millimeter, mono crystal 1 millimeter to 10 millimeter, CVD inserts of a few square millimeter to discs up to 200 millimeter diameter, PCD inserts of a few square millimeter to discs 104 millimeter diameter, cBN grit in micron range 0.1 to 60 micron, in wheel grit range 40 micron to 200 micron, PCBN inserts of a few mm to discs up to 104 mm diameter.

The diamond particles are first coated in a hot coating process to provide an inner layer, which may be a metal layer or a metal carbide, nitride or carbonitride layer. In the case of cBN, such inner coating would typically be a metal nitride or boride or boronitride layer. In this hot coating process, the metal-based coat is applied to the diamond substrate under suitable hot conditions for such bonding to take place. Typical hot coating technologies that can be used include processes involving deposition from a metal halide gas phase, CVD processes, or thermodiffusion vacuum coating or metal vapour deposition processes, for example. Deposition from a metal halide gas phase and CVD processes are preferred.

In processes involving deposition from a metal halide gas phase, the particles to be coated are exposed to a metal-halide containing the metal to be coated (e.g. titanium) in an appropriate gaseous environment (e.g. non-oxidising environments containing one or more of the following: inert gas, hydrogen, hydrocarbon, reduced pressure). The metal halide may be generated from a metal as part of the process.

The mixture is subjected to a heat cycle during which the metal-halide transports the titanium to the surfaces of the particles where it is released and is chemically bonded to the particles.

The outer layer of metal, metal alloy or combination of metals or metal alloys is deposited using a cold coating technique such as low temperature CVD or PVD, which is preferred. It is a low temperature process in that insufficient heat is generated to cause significant carbide formation. Hence, if used alone, it would result in poor adhesion to the diamond particles. An example of a PVD process for applying the outer coating is

PVD sputtering. In this method, the metals, metal alloys or multiple layers of metal are deposited on the inner layer. The sputtering can take place from different positions, using more than one metal/metal alloy. This allows for the production of metallic outer layers that bond better with the bond matrix. They can also be tailored to provide for improved chemical resistance, tailored melt point, and improved resistance to diffusion reactions and the tendency to alloy with the bond matrix.

Examples of coated abrasives of the invention include:

Titanium carbide coating applied by a hot coating process, such as the commercially available SDBTCH, with an outer coating of:

- i) titanium, which improves oxidation resistance,
- ii) tungsten, which provides for improved chemical resistance.

This invention will now be described, by way of example only, with reference to the following non-limiting examples.

## **EXAMPLE 1**

Diamond grit from Element Six, 40/45 US mesh size, was coated in a CVD process to produce TiC coated diamond according to general methods commonly known in the art. The CVD TiC coated diamond was then used as the substrate for the second coating step.

1,000 carats of this TiC coated diamond, 40/45 US mesh size, was placed in a magnetron sputter coater with a rotating barrel. Two small targets of titanium and copper were used with two small independent magnetrons. The coating chamber was evacuated, argon was admitted and the power turned on to form plasma. Sputtering power was increased to 2kW (420V) on the titanium target while rotating the barrel to ensure an even coating on all the diamond particles at 20sccm argon pressure. Titanium was coated for 45 minutes. Copper was simultaneously coated at 100W purely to prevent contaminating the copper target. Power to the titanium target was

-7-

ramped down from 2kW to 100W and at the same time power to the copper target was ramped up from 100W to 2kW, over 30 minutes. Copper was coated at 2kW (540V) for 45 minutes. Titanium was simultaneously coated at 100W purely to prevent contaminating the titanium target. The total coating time was 120 minutes.

An analysis of this coated diamond was undertaken, consisting of X-ray diffraction, X-ray fluorescence, Chemical assay of the coating, Optical and Scanning Electron Microscopy image analysis, and particle fracture followed by cross-sectional analysis on the SEM.

Visually, this coating appeared a dark coppery colour. This colouring appeared evenly distributed over each particle and each particle appeared identical. The coating looked uniform and without any uncoated areas. Observation on the SEM again showed an even coating with a rough morphology composed of agglomerated particles. Fractured particles were also observed on the SEM. A two-layer structure was not easily distinguishable, the complete layer having a thickness of about 0.8 microns. This particular coating resulted in an assay of 2.7%. The TiC coating in this size used for this batch typically has an assay of 0.77%. The rest of the 2.7% is therefore attributable to the PVD TiC and Ti/Cu metal layer on top of the CVD TiC. When analysed using XRD, TiC and Cu metal were found. XRF analysis showed 23% Ti and 77% Cu.

# **EXAMPLE 2**

CVD TiC coated diamond produced in accordance with Example 1 was used as the substrate for the second coating step. 1,000 carats of this TiC coated diamond, 40/45 US mesh size, was placed in a magnetron sputter coater with a rotating barrel. Two small targets of titanium and tungsten were used with two small independent magnetrons. The coating chamber was evacuated, argon was admitted and the power turned on to form plasma. Sputtering power was increased to 2kW (420V) on the titanium target while rotating the barrel to ensure an even coating on all the diamond

particles at 20sccm argon pressure. Titanium was coated for 45 minutes while oscillating the barrel. Tungsten was simultaneously coated at 100W purely to prevent contaminating the tungsten target. Power to the titanium target was ramped down from 2kW to 100W and at the same time power to the tungsten target was ramped up from 100W to 2kW, over 30 minutes. Tungsten was coated at 2kW (450V) for 60 minutes. Titanium was simultaneously coated at 100W purely to prevent contaminating the titanium target. The total coating time was 135 minutes.

An analysis of this coated diamond was undertaken, consisting of X-ray diffraction, X-ray fluorescence, Chemical assay of the coating, Optical and Scanning Electron Microscopy image analysis, and particle fracture followed by cross-sectional analysis on the SEM.

Visually, this coating appeared a dark silvery grey metallic colour. This colouring appeared evenly distributed over each particle and each particle appeared identical. The coating looked uniform and without any uncoated areas. Observation on the SEM again showed an even coating with a slightly rough morphology composed of small agglomerated particles. Fractured particles were also observed on the SEM. A two-layer structure was seen in most instances, the Ti-W layer having a thickness of about 0.2 microns. This particular coating resulted in an assay of 2%. The TiC coating in this size used for this batch typically has an assay of 0.77%. The rest of the 2% is therefore attributable to the PVD TiC and Ti/W metal layer on top of the CVD TiC. When analysed using XRD, diamond, TiC and W metal were found. XRF analysis showed 32% Ti and 68% W.